

Comparison between experiment and calculated band structures for DyN and SmN

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We investigate the electronic band structure of two of the rare-earth nitrides, DyN and SmN. Resistivity measurements imply that both materials have a semiconducting ground state, and both show resistivity anomalies coinciding with the magnetic transition, despite the different magnetic states in DyN and SmN. X-ray absorption and emission measurements are in excellent agreement with densities of states obtained from LSDA+*U* calculations, although for SmN the calculations predict a zero band gap.

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I. INTRODUCTION

Despite several decades of research, many fundamental questions remain about the electronic structure of the rare-earth nitrides (RE-Ns). Both metallic and semiconducting states are found among early measurements, even for materials of nominally the same composition.^{1,2} It has been only recently that realistic band-structure calculations have been performed, and these have heightened the interest by predicting half metallicity in some members of the series.^{3–11} However, describing the highly correlated 4*f* electrons within band theory is a challenging problem, and as yet there is no consensus among the predictions regarding the electronic states. Nevertheless, there is a strong desire to explore these materials, and not only for the contribution to be made to the advancement of band-structure calculation techniques; their properties as strongly spin-polarized conductors, either metallic or semiconducting, can be expected to lead the way to improved materials for spintronics devices.

The most studied of the RE-Ns is GdN,^{6–17} which has an exactly half filled Gd 4*f* shell and possesses the highest Curie temperature of the series. Exchange splitting reduces the gap between the valence and conduction band states for the majority spin, but various treatments disagree about whether the bands actually overlap to give a half-metal^{3,8} or whether a gap persists.^{6,17} The first attempt to calculate the properties of the full RE-N series, based on the local spin density approximation to density functional theory (LSDA) plus a self-interaction correction, found electronic states ranging from half-metallic to insulating.³ More recently an approach based on LSDA plus Hubbard-*U* corrections (LSDA+*U*) has highlighted the importance of the 4*f* electrons' orbital degrees of freedom in the cubic symmetry of the lattice.⁴ There is an urgent need for quality experimental data addressing the band structure against which to compare predictions.

To a large extent the lack of reproducible experimental data is due to the propensity of these nitrides to decompose in the presence of moisture in even very dry atmospheres.^{1,13} Furthermore, it is difficult to ensure a low concentration of

nitrogen vacancies.^{1,15} It is thus important in this respect that recent advances have been made toward the preparation and passivation of near-stoichiometric GdN films.^{13,15} Conductance data on these very recent films have established that GdN is a semiconductor at ambient temperature, and that despite a narrowing of the band gap it remains so in the low-temperature ferromagnetic phase. There exists in addition x-ray absorption spectroscopy results that show features in the conduction band density of states (DOS),¹² and these results have recently been shown to be in good agreement with band-structure calculations.⁹ There is a clear imperative to extend these results to a systematic study of the full band structure across the rare-earth nitride series.

In the present work we describe an experimental study of nitrides of the RE elements with two fewer (Sm) and two more (Dy) 4*f* electrons than Gd. We find excellent agreement between x-ray spectroscopy measurements and recent electronic structure calculations,⁴ confirming the ability of the LSDA+*U* method to describe key aspects of the band structures in these highly correlated materials. However, resistivity and magnetization data show that both materials are semiconducting in their low-temperature magnetic ground states, in agreement with theory for DyN but implying that some fine-tuning of the LSDA+*U* parameters is required for SmN. The understanding of these RE containing compounds and their behavior in x-ray absorption and emission is of interest also in other highly correlated systems such as high-temperature superconductors or colossal magnetoresistance manganites.^{18,19}

DyN, like GdN, is a ferromagnet with a Curie temperature (T_C) reported variously as 17–26 K.^{1,2} SmN, in contrast, is reported to be antiferromagnetic with a Néel temperature (T_N) of 15–18 K,^{1,2} although it should be noted that the moment per Sm ion is very small and the antiferromagnetic assignment has not been confirmed. Recent calculations assuming a ferromagnetic ground state have found that DyN is a semiconductor while SmN is a half metal.^{3,4} The calculated gaps in the paramagnetic phase quoted in Ref. 4 are in reasonable agreement with early optical measurements.¹ The

conductivity of these early samples of SmN and DyN was reported to show semimetallic behavior, although it is certain that these are influenced by imperfect stoichiometry and impurities. There have been no recent reports of the conductivity of SmN or DyN.

II. SAMPLE GROWTH AND CHARACTERIZATION

We have grown films of these two nitrides using the technique developed for GdN, by vacuum evaporation of the RE metals in the presence of a scrupulously pure atmosphere of N_2 at a pressure of 10^{-4} mbar.¹⁵ *In situ* resistance measurements were performed to a minimum temperature of 100 K, and *ex situ* studies performed on films passivated by a layer of nanocrystalline GaN. Consistency between the *in situ* and *ex situ* resistivity results confirms the effectiveness of the capping layers. Rutherford backscattering spectroscopy has established that the films have the correct stoichiometry to within the detection limit of about 2%, and their rocksalt structure has been shown by x-ray diffraction to consist of typically 8 nm crystallites with the expected lattice constants.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the magnetization and resistivity of, respectively, DyN and SmN. Turning first to the magnetization, DyN shows a divergence between the field-cooled and zero-field-cooled data below 25 K. Field sweeps at 5 K show a hysteresis and saturation (see inset), making it clear that the low-temperature phase is ferromagnetic, with the T_C of around 25 K near the top of the range reported in the literature.^{1,2} The response of SmN is much weaker at all temperatures, despite the use of a measurement field of 5000 Oe rather than the 500 Oe used for DyN, and there is an approximately constant offset of about $0.004\mu_B$ per Sm associated with uncertainties in removing the background signal from the Si substrate. Nevertheless, the field-cooled and zero-field-cooled data separate implying a magnetic transition at around 20 K, slightly higher than previously reported transition temperatures.^{1,2} No clear hysteresis is seen at 5 K, so it is likely that SmN is, in fact, metamagnetic (i.e., an antiferromagnet in which the moments can be ferromagnetically aligned by an applied field). Even in a field of 6 T the low-temperature moment is less than $0.1\mu_B$ per Sm, considerably less than the theoretical saturated moment for atomic Sm ions of $gJ\mu_B=0.71\mu_B$. This is consistent with the calculations of Ref. 4 which emphasize the importance of orbital magnetic moment in these materials and for SmN in a ferromagnetic state essentially predict a cancellation of the orbital and spin moment, i.e., $L_z+2S_z=0$.

The magnitude of the resistivity is a factor of 10 greater in DyN than in SmN and the temperature dependence more pronounced, although for both materials the behavior is typical of a heavily doped semiconductor and any activation energy extracted from the data is orders of magnitude smaller than the calculated band gaps. Nevertheless the trends are consistent with the calculated gaps if the energy of the defect states scales with the band gap. Anomalies are seen at the

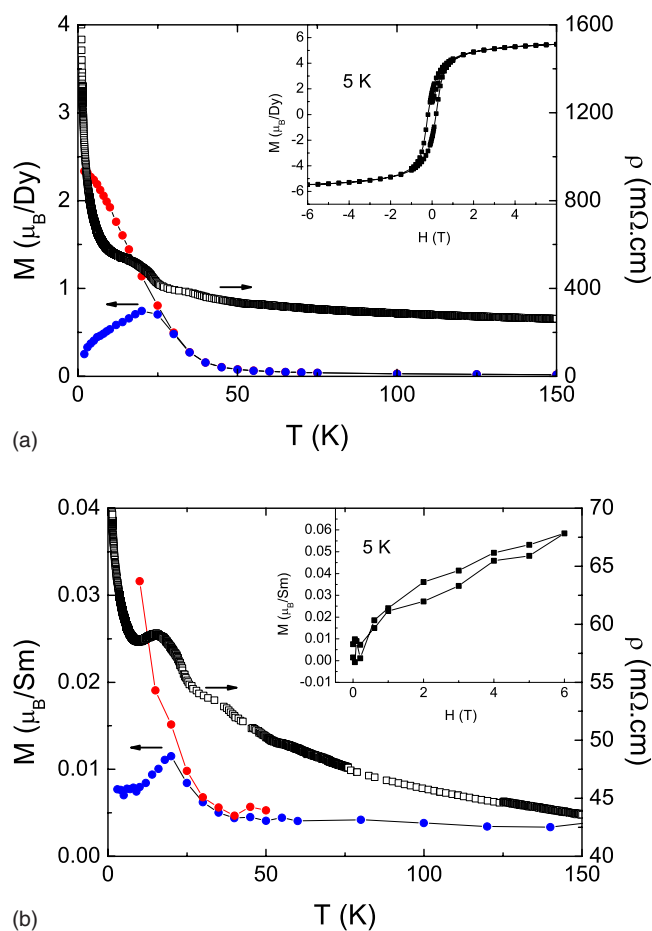


FIG. 1. (Color online) Magnetization and resistivity of (a) DyN and (b) SmN (insets show magnetization versus field at 5 K). Blue symbols show zero-field-cooled magnetization data, and red symbols show field-cooled data.

magnetic ordering temperature, strongly reminiscent of the behavior of GdN in which exchange splitting of the bands causes a reduction in the relevant excitation energy.^{12,15} These measurements are taken at zero field, so in light of the previous discussion it is interesting that the anomaly exists in SmN as well as in ferromagnetic DyN. In any case, the temperature dependence of the resistivity establishes that both materials are semiconducting over the entire temperature range. We now discuss measurements that address the band structure directly.

We have performed x-ray absorption near-edge spectroscopy (XAS) at the N K edge to give a direct measure of the N p -projected empty-state partial DOS (PDOS), complemented with x-ray emission spectroscopy (XES) to plot out the filled-state N p PDOS. For the x-ray spectroscopy the growth was carried out in the preparation chamber on the X1B synchrotron beamline at the National Synchrotron Light Source at Brookhaven National Laboratory, and measurements completed *in situ* without breaking the vacuum. X-ray absorption spectra were recorded using the total electron yield, with the spherical grating monochromator providing an energy resolution of 0.2 eV. X-ray emission spectra were obtained using a Nordgren-type grazing-incidence soft x-ray

spectrometer with a resolution of 0.4 eV. Both XAS and XES were recorded at room temperature.

In Fig. 2 the XAS and XES measurements of the PDOS are displayed, normalized separately to their maximum values. The absolute energies are somewhat arbitrary, but the relative energy scales have been carefully calibrated using the elastic peaks in XES spectra obtained at different excitation energies. Note that, apart from the location of the elastic peak, the XES spectra were insensitive to the excitation energy. The calibration was further confirmed using the known *L*-edge peak positions of a reference Co sample.

The XES looks qualitatively similar in DyN and SmN with both displaying a relatively narrow asymmetric band. The absorption spectra of both materials also exhibit strong similarities, with a broad rise above the absorption edge followed by a series of peaks stretching more than 25 eV. Both DyN and SmN show a clear energy gap between the absorption and emission, which we will discuss in detail below. To further the comparison XAS for GdN obtained from Ref. 12 is also included in the plots. Once again the same set of principal features is present but with slightly lower resolution, presumably due to the use of a Cr capping layer on the GdN.

A comparison with XAS data from a thin film GaN sample containing molecular nitrogen²⁰ showed that the π^* resonance of N₂ appears in the same energy range as peak A, although these features in our RE-N spectra are much too broad to assign solely to the molecular signal. On the other hand a clear N₂ signal appears in the XAS after prolonged beam exposure, and a similar effect was noted for the GdN in Ref. 12 for which peak A is narrower than those in DyN or SmN. Thus, the XAS peak A is intrinsic to the RE-N samples, but some slight interference from molecular N₂ trapped within the films during growth may also be present.

To extract information about the band structure we include in Fig. 2 the calculated PDOS for all three materials obtained from detailed band-structure calculations. The PDOSs were calculated using the full-potential linearized muffin-tin orbital²¹ (LMTO) method within the LSDA+*U* approach.^{4,6,22} The Hubbard-*U* correction applied to the RE 4*f* states is based on previous brehmsstrahlung isochromat spectroscopy (BIS) and x-ray photoelectron spectroscopy (XPS) studies of Gd compounds, and the expected scaling of the screened *U_f* with the bare Coulomb interactions in the other REs taken from atomic calculations. The trend in *U_f* values was discussed in Ref. 4. An additional shift is applied to the RE 5*d* states, although here *U_d* is used to correct essentially different physics, namely, the usual underestimate of the gap in semiconductors. In the present materials, this leads to a shift in RE-*d* states. The *U_d* value for GdN was recently revisited based on a new study of the optical properties and submitted as a separate paper,²³ but we note that the revised *U_d* does not alter significantly the shape of the conduction band N *p*-like PDOS or the comparison to XAS. For SmN and DyN optical data are not yet available, and thus the same *U_d* value was used as in Ref. 4. For comparison to the room temperature experimental data the calculated PDOSs have been summed over the two spin orientations.

The measured gap between the XAS and XES is about 1.5 eV for DyN and SmN, about 1 eV larger than the calcu-

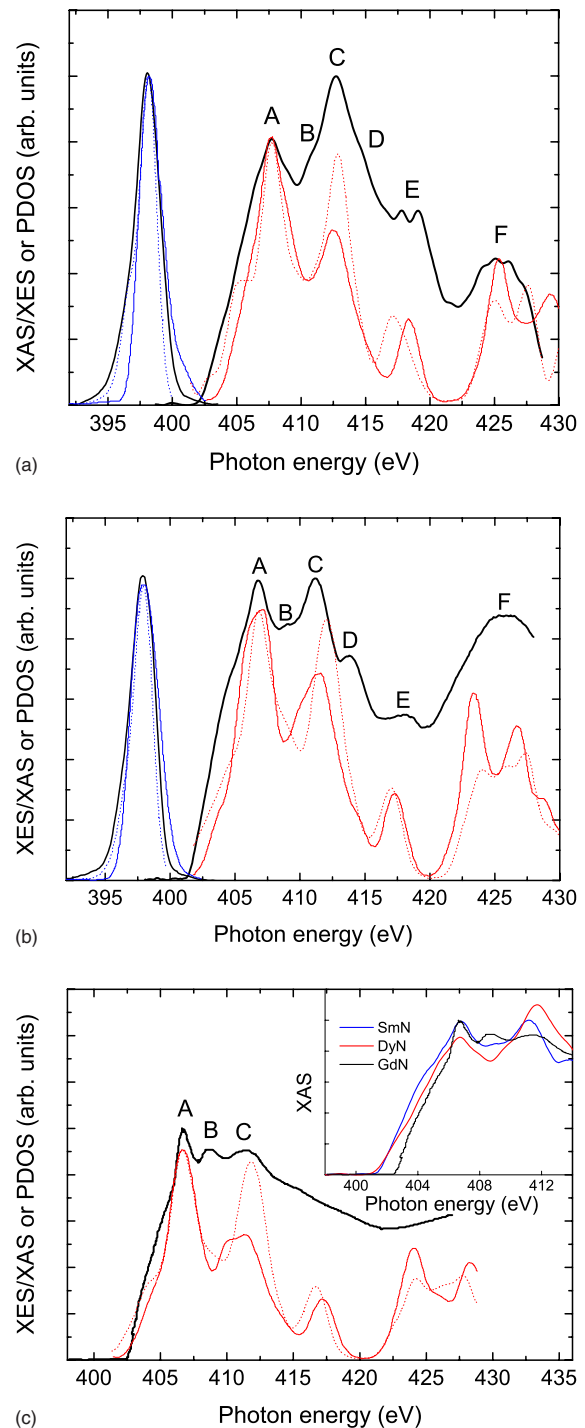


FIG. 2. (Color online) Measured x-ray absorption (thick black line) and emission (thin black line) for (a) DyN, (b) SmN, and (c) GdN (Ref. 12), compared to the calculated nitrogen PDOS. The calculations are performed both with (solid lines) and without (dotted lines) including the core hole. The inset to (c) compares the measured absorption for all three materials.

lated values quoted above. However, XAS creates a core hole that shifts the measured spectra by uncertain amounts dependent on the degree of screening and the projection of the states onto the core hole. In fact, analysis of the dynamical many-body effects in model systems suggests that the

correct potential to use for the absorption includes the core hole on the absorbing atom, while for emission the correct potential is that without the core hole^{24,25} (the “final-state rule”). Others have found that the best description is achieved somewhere between the initial- and final-state rules and have suggested that it depends on whether the system is metallic or insulating.²⁶ Calculations for both potentials are included in Fig. 2, where the core hole case was calculated using a simple cubic cell with a basis in which every fourth nitrogen atom has a core hole. In light of this we do not attempt to compare the measured and calculated gaps, but instead adjust the energy axis of the calculated filled and empty states separately to best match the experiment.

The calculation with no core hole gives an excellent description of the valence band N p PDOS, including the asymmetry on the low-energy side. In contrast note the presence of a shoulder on the high-energy side of the calculation that includes the core hole which is clearly not present in the experiment. Thus we can confirm the accuracy of the band-structure calculation and the obedience of the final-state rule for the valence band. Note that the calculation predicts a small contribution to the bottom of the band associated with hybridization between nitrogen $2p$ states and the highest occupied RE $4f$ states. There is spectral weight at the bottom of the XES which may be attributed to this, although with the present experimental resolution it is difficult to be certain. A comparison with XES data from GdN, which lacks such states, would be interesting in this respect.

For the XAS, the core hole calculation provides a remarkably good fit, reproducing even the high-energy features E and F in DyN and SmN. There are also shoulders hinting at peak B for GdN and the weak features B and D for SmN. This provides strong evidence that the present band-structure calculation correctly describes the unfilled density of states for these RE nitrides. It should be noted that the calculation with no core hole also performs well, and looks quite similar to the core hole calculation, in contrast with recent results obtained for GaN.²⁷ This is largely due to the fact that the N p PDOS in the conduction band can be interpreted rather as the p component of a partial wave expansion inside the N sphere of the tails of the predominantly RE d -like and some RE f -like atomic states extending into the N spheres. Thus, they are not as sensitive to the perturbation of the core hole as the XES. This explanation is based on the LMTO terminology.^{28,29} Alternatively, in a linear combination of atomic orbitals point of view, the conduction bands are anti-bonding combinations of RE d (and RE f) orbitals with N p orbitals. Their energy difference implies that the higher states have only a small N p contribution and it is precisely this contribution we are measuring.

To further investigate systematic variations across the RE-nitride series the absorption edges of all three materials are compared in the inset to Fig. 2(c). Here, the energy axes have

been adjusted to align the peaks A, which are calculated to lie at a similar energy above the Fermi level in each case. There are differences between the peak locations and relative peak strengths, which should form a useful guide for any subsequent refinement of the band-structure calculations. The absorption onset for GdN is also pushed up in energy relative to DyN and SmN. This can be interpreted as evidence of unoccupied bands of low dispersion and high RE f character just above the Fermi level in SmN and DyN, which provide the major contribution to the N p PDOS in this energy region. Such states are not expected for GdN.^{4,9}

IV. CONCLUSIONS

In summary, we have provided much needed experimental data addressing the band structure of two of the rare-earth nitrides, namely, DyN and SmN. Our x-ray spectroscopy data confirm the ability of LSDA+ U calculations to reproduce the main features of their band structures, although some fine-tuning may be required to reproduce the band gaps implied by resistivity data. It should be noted in this context that the calculated gap depends sensitively on the U_d parameter which controls the position of the RE- d bands and was adjusted in the calculations to the optical absorption threshold in GdN reported by Hulliger *et al.*¹ and identified with the average of spin-up and spin-down direct transitions at the X point. Experimental studies of the optical absorption threshold for DyN and SmN are planned and may assist in the determination of this U_d parameter in the LSDA+ U theory.

We note also the contribution that might be made by XPS or BIS to understanding the band structure of these materials. These techniques probe the total density of states, and have proven useful for investigating the location of the $4f$ levels in various gadolinium pnictides,¹¹ but to our knowledge no data presently exist for SmN or DyN.

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